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Form Approved  
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE See Title Page		3. REPORT TYPE AND DATES COVERED 1 February 1987 to 31 January 1991	
4. TITLE AND SUBTITLE Use Title on Reprint One Copy of Each Submitted				5. FUNDING NUMBERS N00014-87-C-0146 0R0A444C- 43051 43051S4	
6. AUTHOR(S) See Individual Articles				8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Vanderbilt University Nashville TN 37332 (615-322-2786)					
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5660				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Each Paper Summarized on first page. Journal articles submitted as contract reports. All work performed under Government contract.					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See first page of Article					
14. SUBJECT TERMS Free Electron Lasers    Medicine    Biology Biomedical Instrumentation Energy    Cells				15. NUMBER OF PAGES 00	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL		

19960104 062

Scientific and Technological Applications of Free-Electron Lasers  
in Ultraviolet Photon-Stimulated-Desorption Spectroscopy

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ABSTRACT

Recent synchrotron light sources suggest that VUV and XUV free-electron lasers could provide new spectroscopic tools for studying photon-surface interactions and simultaneously drive needed developments in ultraviolet optics technology.

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Justification _____	
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Discussions of photon-surface interactions have traditionally been cast in terms of the collective properties (*e.g.*, the heat capacity or the optical susceptibility) of the irradiated material. However, the development of lasers and synchrotron light sources, coupled with innovative applications of both mass and optical spectroscopy, is making it possible to study photon-surface interactions at an atomic scale by determining the quantum states of atoms and molecules at and near material surfaces. Short-wavelength free-electron lasers operating in the XUV and VUV regions of the spectrum offer some exciting prospects for novel photon-matter interaction experiments which take advantage of the FEL's intrinsic properties of narrow bandwidth, high intensity, short temporal pulse length and coherence. In this review, we examine some of the ways in which free-electron lasers in the VUV and XUV can lead both to new tools for studying photon-surface interactions through uv-photon-stimulated-desorption (PSD) spectroscopy, and to new developments in optical technology which might help solve certain pressing technological needs of XUV FELs.

Much of the interest in PSD spectroscopy in the last decade has been focussed on the specific electronic mechanisms through which incident electronic energy is absorbed, localized and ultimately transformed or dissipated into luminescence, creation of electron hole pairs, and, in some cases, into kinetic energy of desorbing atoms or molecules. The early work of Knotek and Feibelman [1] showed, for example, that the desorption of oxygen ions from titania surfaces was made possible by a specific core-level excitation which led to the creation of stable hole pairs on individual ions, with the subsequent Coulomb deformation of the lattice

providing the energy needed to expel the oxygen ion. A key element in elucidating that particular mechanism was the identification of the specific core levels which were excited -- an identification made possible by the availability of tunable synchrotron light.

The energy of a specific atomic core level is relatively easy to pinpoint in an excitation spectrum, even with the relatively coarse wavelength tunability provided by a synchrotron light source. However, in dealing with molecular desorption processes of interest in surface chemistry and catalysis, where energy may be shared among many competing levels, is much more difficult. Synchrotron sources do not presently provide the intensity needed for many important experiments, and the bandwidth of the synchrotron light is often too large to resolve molecular levels. However, an XUV or even VUV free-electron laser, with its high intensity and much narrower bandwidth, would make it possible to provide similarly detailed information about the flow of energy in molecular desorption. A particularly tantalizing example of the possibilities here has been furnished by recent work in our laboratory on electron-stimulated desorption of OH from surfaces [2]. The rotational distribution of the excited OH is distinctly non-Maxwellian, suggesting an electronic rather than a thermal origin for the desorption. However, the electron-induced excitation is not state-specific enough to allow the identification of the entrance-channel states of the excited OH molecules. The use of a tunable VUV FEL would allow identification of the precise entrance channels leading to the formation of excited OH, and remove much of the guesswork from attempts to ferret out the desorption mechanism. In addition, the spectrum of light emitted by excited OH should show entrance-channel polarization effects because of the symmetry imposed on the single hole in the OH electronic shell structure by the presence of the surface; here again, the ultraviolet FEL could provide detailed state selection in the entrance channel which would help to pinpoint the dynamics of the desorption process.

Matrix isolation spectroscopy furnishes another intriguing example of the possibilities for an ultraviolet FEL, this time because of the FEL's ability to generate tunable, narrowband

radiation in a region of the spectrum where synchrotron sources are not particularly efficient. In synchrotron radiation experiments on KCl crystals, we have identified a characteristic band of vibrational transitions of the  $\text{CN}^-$  radical from a metastable excited state in the ultraviolet [3]. The  $\text{CN}^-$ , well known as a pseudo-halide and substitutional impurity in bulk alkali halide studies, appears in this case to be bound to the surface as if it were a gas of non-interacting molecules. In carrying out an excitation function measurement, we found a sharp peak at 7 eV and significant fine structure superimposed on a broader peak at synchrotron photon energies above 12 eV. The 7 eV peak is a barely resolved doublet, and matches the position of a transition known from molecular computations. However, the transition cannot be studied in gas phase, because it is above the autoionization limit; it is also impossible to see the transition in the bulk, because coupling to the crystal lattice quenches the excitation before radiation occurs. Thus it is apparently possible to have a kind of two-dimensional matrix isolation spectroscopy for many important molecules, in which the binding to the surface is just sufficient to depress certain high-lying excited states below the conduction band. While synchrotron radiation is a relatively imprecise probe for studying molecular transitions in the matrix-isolated species, the XUV or VUV free-electron laser, once again because of its narrow linewidth and tunability, would be an ideal tool.

In addition to these novel spectroscopic applications of the proposed ultraviolet free-electron lasers, photon-stimulated desorption spectroscopy with XUV-VUV FELs could also contribute directly to the solution of a pressing problem in FEL optical technology: the identification of the fundamental mechanisms for damage to XUV and VUV optics. We have argued elsewhere [4] that laser-surface interactions are generically related to the process of desorption induced by electronic transitions (DIET), a phenomenon triggered in exemplary fashion by both photons and electrons. At the atomic or molecular scale, an understanding both of the desorption rates and of the effects of desorption on surface composition and electronic structure, would help immeasurably in identifying the underlying physics of the laser

damage mechanisms. Recent work with synchrotron radiation has shown, for instance, that under certain circumstances, hydrogen appears to inhibit DIET of excited-state atoms; apparently the weak physisorption of hydrogen is still sufficient to change the electronic structure of alkali halide surfaces in a way which prevents the formation of excited, energetic alkali atoms. However, whether the hydrogen inhibits desorption of ground-state alkali atoms, which are by far the most numerous desorption products [5], or of the halogen atoms, remains to be seen. Free-electron lasers operating in the vacuum or extreme ultraviolet could provide a new tool for studying this phenomenon because of their ultrashort pulse structure and their ability to tune through specific entrance-channel excitations leading to the formation of self-trapped excitons, permanent mobile defects, and ultimately to desorption. In this case, then, the FEL provides a state-specific, impulse excitation whose relaxation through many different channels could be followed in both time- and spectrally-resolved fashion. While the vigorous efforts now going on to develop damage resistant ultraviolet optics will certainly bring significant improvements in performance, "state-to-state" measurements of this type will be required to make significant breakthroughs in fabricating damage-resistant uv optics.

The synchrotron light source has brought significant new scientific and technological developments from a deeper understanding of photon-surface interactions. The prospect of free-electron lasers operating in the VUV and XUV -- with the tunability of synchrotron sources and the additional advantages of high intensity, coherence, and narrow bandwidth -- are likewise certain to create novel and exciting classes of photon-surface studies.

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